LOCALIZATION OF EMPTY 4p ORBITALS IN CERTAIN TRANSITION METAL COMPOUNDS*

K. P. SINHA

NATIONAL CHEMICAL LABORATORY, POONA-8

AND

CHINTAMANI MANDE

DEPARTMENT OF PHYSICS, POONA UNIVERSITY, POONA-7

(*Received November 5, 1962*)

ABSTRACT. The splitting of the K x-ray absorption edge of certain transition metal ion compounds with a tetrahedral co-ordination is explained on the basis of ligand field theory. It is pointed out that in the tetrahedral configuration the empty $4p$ orbitals of the metal ion are localised whereas in octahedral surroundings these form strong bonding and antibonding molecular orbitals with the appropriate combination of ligand orbitals. The antibonding empty orbital (t^*_{1u}) to which the first x-ray transition takes place is delocalised

These conclusions are consistent with observations.

INTRODUCTION

The existence of localized empty orbitals in solids is expected to play an important role in several physical processes such as optical absorption, electrical properties, and magnetic exchange interactions (Sinha 1961). X-ray absorption spectroscopy provides a powerful method of studying the nature of empty orbitals in solids (Cauchois, 1948; Mande, 1960). Several workers have investigated the K absorption spectra of transition metal ions in their various physico-chemical states (See Wilkinson and Cotton, 1959 for details).

Recently, van Nordstrand (1960) has reported a large number of K absorption curves of transition metal ions in different types of solids. He classifies these curves in four categories, namely, type I spectra, associated with an octahedral coordination in the common salts, hydrates, complexes and oxides; type II, associated with octahedral coordination shell constituted of linear ligands such as CN or CO; type III characteristic of metals and metallic phases; and type IV, associated with tetrahedral configurations (e.g. $KMnO_4$). These four typical spectral curves are shown in Fig. 1.

Of these, the type IV curve alone shows the splitting of the principal absorption edge. Collet (1959) has also reported a similar splitting in NiK absorption in the complex $K_2[Ni(CN)_4]$, where the ligands form a square planar configuration.

* Communication No. 516 from the National Chemical Laboratory, Poona-8 (India).

The first maximum in the principal absorption edge (in type IV) may be interpreted as a transition of a 1s electron towards an empty $4p$ orbital.

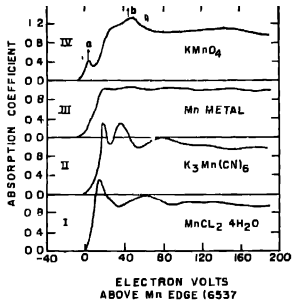

Fig. 1. Four different types of K absorption spectra of manganese in varying chemical states as given by R. A. Van Nordstrand The markings 'a' and 'b' are by the present authors. 'a' represents the x-ray transition $1s \rightarrow 4p$, and 'b' $1s \rightarrow p$ limit

The purpose of this note is to point out and interpret theoretically the occurrence of localized $4p$ levels in certain compounds with tetrahedral configuration around the transition metal ion, which in turn, is responsible for the splitting of the absorption edge. We also explain the absence of the same in octahedral systems. A purely electrostatic crystal field calculations by Cotton and Ballhausen (1956) lead to somewhat different conclusions.

THEORETICAL CONCEPTS AND DISCUSSION

In this section, we discuss results of our theoretical calculations for $KMnO_4$ which is a typical example of a transition metal ion in tetrahedral configuration i.e. (MnO_4)—. In formulating the electronic configuration of the tetrahedron, we also include the electrostatic crystal field effects of the surrounding nearest K^+ ions. For the $(MnO_4)^-$ tetrahedron itself, we follow the molecular orbital approach. The results obtained would apply equally well to other similar systems.

The position of the K^+ ions were taken from the crystallographic data of Mooney (1931) on $KMnO_4$. The effective crystal field potential can be expressed, following the general method due to Bethe (1929), as

$$V(6K^+) = C_0^0 Y^0_0 + C^0_2 r^2 Y^0_2 + C^1_2 r^2 (Y^1_2 + Y_2^{-1}) + C_2^2 r^2 (Y_2^2 + Y_2^{-2}) + \ldots \qquad (1)$$

where C's are the coefficients, Y's the spherical harmonics and r the radial co-ordinate. Since we are concerned with the splitting of the $4p$ levels only terms upto second order spherical harmonics have been included in (1).

The calculation shows that the term $C_0^0 Y^0_0$ gives a constant depression of all the energy levels of Mn by about 20 eV. For an electron in $4p$ orbitals, the other

terms in (1) give rise to a splitting of p_x, p_y, p_z orbitals by approximately 0.2 eV which is comparatively small.

In order to study the influence of the inner oxygen atoms on Mn in $(MnO_4)^-$, we treat the inner ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$) electrons of Mn as constituting the ion core and only $3d^5\ 4s^2$ electrons are supposed to be involved in covalency. The appropriate orbitals to be considered for covalency are, however, $3d$, $4s$ and $4p$. Likewise, for oxygen we take the $1s^2\ 2s^2$ electrons as forming the ion core and the remaining $2p^4$ electrons participate in bonding. The three oxygen p orbitals are p_σ, π_1 and π_2 the former pointing towards the central ion. We classify the central ion valence orbitals and the linear combination of oxygen ion p orbitals, which interact strongly according to the point symmetry group T_d, following Wolfsberg and Helmholz (1952) The metal ion orbitals span the irreducible representation (given in brackets) as indicated · i.e $s(A_1)$; d_γ : d_z2, $d(x^2-y^2)$ (E); p_x, p_y, p_z; d_C ; d_{yz}, d_{zx}, d_{xy}, (T_2). The linear combinations of the ligand p_z orbitals span the representations. $(\sigma_1+\sigma_2+\sigma_3+\sigma_4)/2$. A_1; $(\sigma_1+\sigma_2-\sigma_3-\sigma_4)/2$, $(\sigma_1-\sigma_2+\sigma_3-\sigma_4)/2$, $(\sigma_1-\sigma_2-\sigma_3+\sigma_4)/2$. T_2. Likewise, there will be combinations of π orbitals belonging to different representations. The strength of the bonding and antibonding molecular orbitals formed between the metal ion and the ligand orbitals is determined from symmetry, relative energies and overlap considerations. It is seen that s, d_γ and d_ε form strong bonding and antibonding orbitals with the appropirate anion molecular orbitals. The bonding with the $4p$ orbitals is not strong as can be visualized from overlap considerations and that d_ε orbitals also compete strongly for the same purpose. Thus in effect the $4p$ orbitals of the metal ion remain more or less of the atomic type and remain empty along with other antibonding orbitals. The x-ray absorption at 'a' in Fig. 1 is interpreted as $1s$ to $4p$ transition with the latter remaining localized.

Let us now consider the transition metal ion in octahedral configuration i.e. the metal ion surrounded by six ligands (e g. O^{2-} or CN). The point symmetry group is O_h. The metal ion orbitals outside the closed shell configuration are again $3d$, $4s$, $4p$ and span the irreducible representations as indicated i.e. $4s(A_{1g})$, $3d_\varepsilon$ (T_{2g}), $3d_\gamma$ (E_g) and $4p(T_{1u})$. The appropriate linear combinations of the six ligand p_σ orbitals span the representations A_g E_g, T_{1u} (Orgel 1960). Here too, we disregard the effect of π orbitals. Thus the strong bonding and antibonding orbitals are due to the mixing of $3d_\gamma$, $4s$ and $4p$ orbitals of the metal ion with the appropriate combinations of the p_σ orbitals of the ligands. In contrast to the tetrahedral case, the $4p$ orbitals in the octahedral configuration are subjected to a strong end on overlap with ligand p_σ orbitals. Thus the antibonding combination t^*_{1u}, which is invariably empty in most systems, is extensively delocalized in octahedral configurations. Also, in the octahedral case there is no set of $3d\varepsilon$ type orbitals of the central ion belonging to T_{1u} symmetry to compete with $4p$ orbitals of the same. In the tetrahedral case, it was shown that the d_ε orbitals

were strongly bonded with the ligand orbitals and this competition also favoured in rendering the $4p$ orbitals localized.

We visualize that in octahedral systems the x-ray transition is from $1s$ to t_{1u}^*, the later being delocalized as well as pushed upwards in energy scale. This would be consistent with the observed spectra in octahedral system where there is no splitting of the principal absorption edge. The effect of the positive ions (e g. K^+) around the octahedron would be similar to the tetrahedral case; however, the magnitude of the constant depression and splitting of the energy levels would depend on the distances and dispositions of these ions. In complex systems such as Mn_3O_4 (distorted spinel structure) where there are two octahedrally surrounded and one tetrahedrally surrounded metal ions, the effect of the tetrahedron is probably diluted owing to the preponderance of the octahedral ions.

CONCLUDING REMARKS

In the foregoing section, we have made tentative suggestions as to why $4p$ empty orbitals of transition metal ions become localized in tetrahedral systems and delocalized in octahedral surroundings. The above conclusion correlates well with the observed K X-ray absorption spectra in such systems. Detailed theoretical calculations and extensive experimental work are in progress and their results will be reported later.

ACKNOWLEDGMENTS

We are grateful to Dr. L. M. Pant for helpful discussions. Our thanks are also due to Dr. A. B. Biswas and Dr. M. W. Chiplonkar for their interest in the work.

REFERENCES

Bethe, H. A., 1929, *Ann. der Phys.*, **3**, 181.

Cauchois, Y., 1948, *Les Spectres de rayons x et la structure electronique de la matiere, Gauthier—Villars, Paris.*

Collet, V.,1959, *Thesis, Paris, Gauthier—Villars.*

Cotton, F. A. and Ballhansen, C. J., 1956, *J. Chem. Phys.*, **25**, 617.

Mande, C., 1960, *Ann. de Phys.* (*Paris*), **6**, 1559.

Mooney, R. C. L., 1931, *Phys. Rev.*, **37**, 1306.

Orgel, L. E., 1960. *An Introduction to Transition Metal Chemistry, Methuen, London.*

Sinha, K. P., 1961, *Ind. J. Phys*, **35**, 484.

Von Nordstrand, R. A., 1960, *Conf. Non-crystalline solids*, John Wiley and Sons, New York.

Van Nordstrand, R. A., 1960, *Advances in Catalysis*, Vol. **12**, Academic Press, New York.

Wilkinson, G. and Cotton, F. A., 1959, *Progress in Inorganic Chemistry*, Vol. **I**, Interscience, New York.

Wolfsberg, M. and Helmholtz, L., 1952, *J. Chem. Phys.*, **20**, 837.